

[English Translation of Excerpt from Reference 3]

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[Title of Invention] ETCHING METHOD AND DEVICE,

MANUFACTURING METHOD FOR SEMICONDUCTOR DEVICES
USING THE SAME AND SEMICONDUCTOR DEVICES

--- (omitted) ---

[Claims]

[Claim 1] An etching method, characterized in that the method comprises a step of preparing a substrate having a membrane comprising an inorganic matter and formed on its surface; and a step of wet etching said membrane on said substrate by the oxygen-involved reaction of oxidation-reduction using a liquid etching agent containing an oxidizing agent having an oxidation-reduction potential of no less than 2V.

[Claim 2] The etching method according to Claim 1, characterized in that said inorganic matter is a poorly water-soluble substance and said reaction of oxidation-reduction is a reaction of generating an easily water-soluble or volatile substance from said inorganic matter.

[Claim 3] The etching method according to Claim 1, characterized in that said inorganic matter is a strontium ruthenium oxide which can be decomposed by said reaction of oxidation-reduction to easily water-soluble or volatile strontium oxide and ruthenium compound.

[Claim 4] The etching method according to Claim 1, characterized in that said liquid etching agent is ozone water having a concentration of no less than 5ppm as delivered to said membrane.

[Claim 5] The etching method according to Claim 1, characterized in that the step of wet-etching said membrane is a step wherein said substrate having said membrane comprising said strontium ruthenium oxide is rotated at a rate of no less than 1000rpm and said ozone water is directly injected onto

said substrate.

[Claim 6] The etching method according to Claim 1, characterized in that said liquid etching agent is ozone water having a concentration of no more than 100ppm as delivered to said membrane.

[Claim 7] An etching device, comprising:

a substrate-rotating mechanism for rotating a substrate treated and having a membrane comprising an inorganic matter at a rotary rate of no less than 100rpm; and

an ozone water-supplying mechanism disposed on said substrate-rotating mechanism for supplying ozone water having a concentration of no less than 5ppm onto the surface of said substrate treated for etching said substrate treated.

[Claim 8] The etching device according to Claim 7, characterized in that said ozone water-supplying mechanism supplies said ozone water to the center of said substrate treated or an adjacent location thereof.

[Claim 9] The etching device according to Claim 7, characterized in that said substrate-rotating mechanism rotates said substrate treated at a rotation speed of no less than 1000rpm.

[Claim 10] A manufacturing method for a semiconductor device, characterized in that the method comprises:

a step of forming a first metal oxide membrane on a semiconductor substrate;

a step of forming a second metal oxide membrane on said first metal oxide membrane;

a step of forming a protective membrane having a desired opening on said second metal oxide membrane; and

a step of etching said second metal oxide membrane exposed from said opening with an ozone-containing aqueous solution;

while at least one of elements among metallic elements forming said first metal oxide membrane contains a poorly water-soluble oxide and all the respective metal elements forming said second metal oxide membrane contain easily water-soluble or volatile oxides.

[Claim 11] The manufacturing method for a semiconductor device according to Claim 10, characterized in that said second metal oxide membrane comprises a strontium ruthenium compound which can be decomposed in said etching step to easily water-soluble or volatile strontium oxide and

ruthenium compound.

[Claim 12] The manufacturing method for a semiconductor device according to Claim 11, characterized in that said ozone water-containing water solution is ozone water having a concentration of no less than 5ppm as delivered to the surface of said second metal oxide membrane.

[Claim 13] The manufacturing method for a semiconductor device according to Claim 11, characterized in that said etching step is a step wherein said substrate having said second metal oxide membrane comprising said strontium ruthenium oxide is rotated at a rate of no less than 1000rpm and said ozone water is directly injected onto said substrate.

[Claim 14] A semiconductor device, characterized in that the device comprises:

an insulation layer having a trench;

a first metal oxide layer formed on the internal surface of said trench;

a second metal oxide layer formed on the internal surface of said trench with the intervention of said first metal oxide and extending to the upper surface of said insulation layer;

a third metal oxide layer embedding the inside of said trench with the intervention of said first metal oxide layer and said second metal oxide layer and extending to the upper surface of said insulation layer on the peripheral edge of said trench with the intervention of said second metal oxide layer; and

a masking layer formed on said third metal oxide layer while said masking layer is at least to cover said third metal oxide layer.

[Claim 15] The semiconductor device according to Claim 14, characterized in that the external edge of said third metal oxide layer is formed on the inside from the external edge of said masking layer while a difference thereof is set to be no more than $0.3\ \mu\text{m}$.

[Claim 16] The semiconductor device according to Claim 14, characterized in that said third metal oxide layer comprises a strontium ruthenium oxide layer.

--- (omitted) ---

[0031] (First Embodiment of Invention) Figure 1 is a cross sectional chart of a nozzle section in a single wafer etching device according to the first embodiment of the present invention, schematically showing a substrate treated wherein membranes to be etched have been formed and their

alignment. A substrate treated (1) which is used in the present embodiment has a flat surface-type capacitor comprising a laminated structure which has been successively formed from a SrRuO membrane (12), a BaSrTiOx membrane (13) and a SrRuO membrane (14). Herein, the semiconductor substrate (11) has the diameter of 8 inches and the thickness of 750 μ m, and respective layers in the laminated structure are 50/40/50nm thick from the lower layer. On the surface of the SrRuO membrane (14), a Teflon-made nozzle head (2) is disposed with the intervention of a stainless steel-made scanning nozzle (3) to have a nozzle front directed toward the SrRuO membrane (14). Out of the front of this nozzle head (2), ozone water (4) as an oxidizing agent is to be injected. The ozone water (4) to be used is based on ultra-pure water and has an ozone concentration of no less than a few ppm.

... (omitted) ...

[0036] Now, ozone water (4) is supplied as emitted from a nozzle head (2) to a neighborhood of the central portion of a substrate treated (1) at a single wafer etching device shown in Figure 1. Herein, the etching condition is set as follows: the rotation of wafer table loading a substrate treated (1) at 2000rpm; the ozone concentration in the ozone water (4) at 10ppm; the flow rate at 1~2 liters/min., and the SrRuO membrane (14) is processed with this treatment for 3 minutes. Subsequently, a resist (21) is stripped with an oxygen plasma stripper by ashing [refer to Figure 2(c)]. A no more than 5 μ m L/S (line and space) pattern can be processed in this manner.

... (omitted) ...

[Brief Description of Figures]

[Figure 1] A cross sectional chart of a nozzle and a substrate section for the explanation of an etching method according to the first embodiment of the present invention.

[Figure 2] A cross sectional chart of a substrate treated for the stepwise explanation of an etching method according to the first embodiment of the present invention.

[Figure 3] A characteristic chart showing relationship between ozone water concentrations and etching rates of SrRuO membrane according to the first embodiment.

[Figure 4] A schematic chart showing the constitution of a single wafer etching apparatus used in the experiment of optimizing the rotary speed of wafer in the etching method according to the first embodiment.

[Figure 5] A chart comparatively showing profiles of the membrane thicknesses of SrRuO membrane along the wafer diameter direction before and after etching.

[Figure 6] A chart comparatively showing profiles of the membrane thicknesses of BaSrTiOx membrane along the wafer diameter direction before and after etching.

[Figure 7] A chart showing the profiles membrane thickness along the diameter direction when SrRuO membrane formed as a single layer on a flat wafer is etched while being rotated at 3 kinds of rotation speeds.

[Figure 8] A cross sectional chart stepwise showing a production method for a capacitor according to the second embodiment of the present invention.

[Code Explanation]

(1) Substrate treated; (2) Scan nozzle; (4) Ozone water; (11) Semiconductor substrate; (13) SrRuO membrane; (13) BaSrTiOx membrane; (14) SrRuO membrane; (21) Resist; (41) Wafer table; (101) Oxide membrane; (102) Trench; (103) SrRuO electrode; (104) BaSrTiOx membrane; (105) SrRuO electrode; (106) TiN masking; (111) W plug electrode; and (112) TiN barrier layer.

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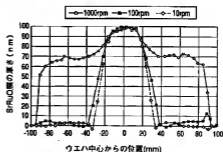
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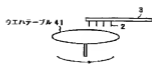
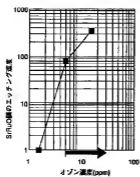
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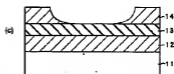
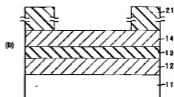
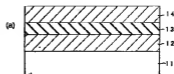
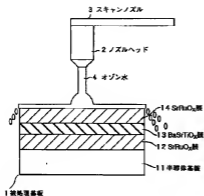
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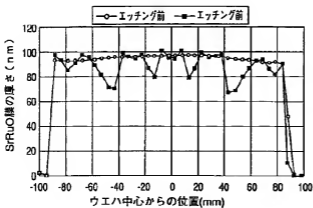
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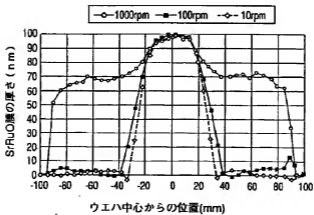
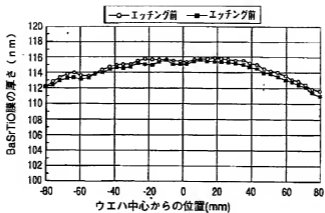






11—半導体基板、12—SrRuO₃膜、13—BaSrTiO_x膜
14—SrRuO₃膜、21—レジスト







(a)



(c)



(b)



(f)



(e)



(g)



(d)



(h)

101…酸化膜、102…トレンチ、103…SrRuO₂電極
 104…BaSrTiO₃膜、105…SrRuO₂電極
 106…TiNマス、111…Wプラグ電極、112…TiNのバリア層